



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

Lewis

(NASA-Case-LEW-11726-1) TWISTED
MULTIFILAMENT SUPERCONDUCTOR Patent

(NASA) 6 p

N73-26752

CSCL 20L

REPLY TO
ATTN OF:

Unclass

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TO: KSI/Scientific & Technical Information Division
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General Counsel for
Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code KSI, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 3,737,824

Government or
Corporate Employee : U.S. Government

Supplementary Corporate
Source (if applicable) : _____

NASA Patent Case No. : CEW-11726-1

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

Yes

No

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of column No. 1 of the Specification, following the words ". . . with respect to an invention of . . ."

Elizabeth G. Carter

Elizabeth A. Carter

Enclosure

Copy of Patent cited above



United States Patent [19]
Coles

[11] **3,737,824**
[45] **June 5, 1973**

[54] **TWISTED MULTIFILAMENT
SUPERCONDUCTOR**

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[73] Assignee: **The United States of America as
represented by the Administrator of
the National Aeronautics and Space
Administration, Washington, D.C.**

[22] Filed: **Aug. 11, 1972**

[21] Appl. No.: **280,031**

[52] U.S. Cl. **336/200, 29/599, 156/18,
174/DIG. 6, 336/DIG. 1**

[51] Int. Cl. **H01v 11/06**

[58] Field of Search **174/DIG. 6, 15 C,
174/126 R, 126 CP; 336/200, DIG. 1;
335/216; 29/599; 156/18**

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Manning et al.*

[57]

ABSTRACT

Masking selected portions of a ribbon and forming an intermetallic compounds on the unmasked portions by a controlled diffusion reaction produces a twisted filamentary structure. The masking material prohibits the formation of superconductive material on predetermined areas of the substrate.

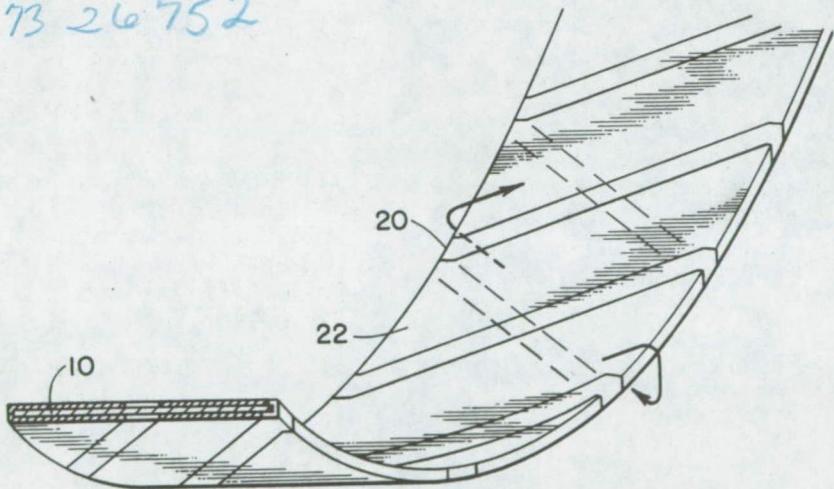
[56] **References Cited**

10 Claims, 8 Drawing Figures

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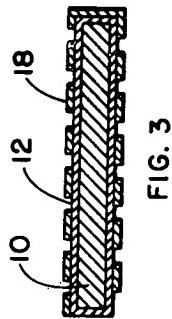


FIG. 3

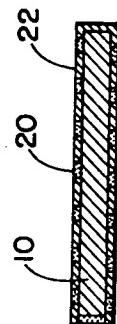


FIG. 6

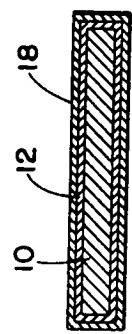


FIG. 2

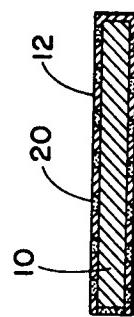


FIG. 5

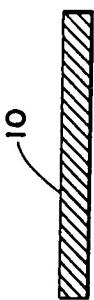


FIG. 1

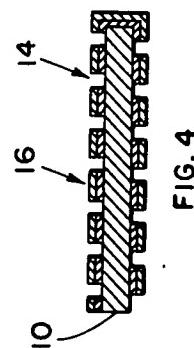


FIG. 4

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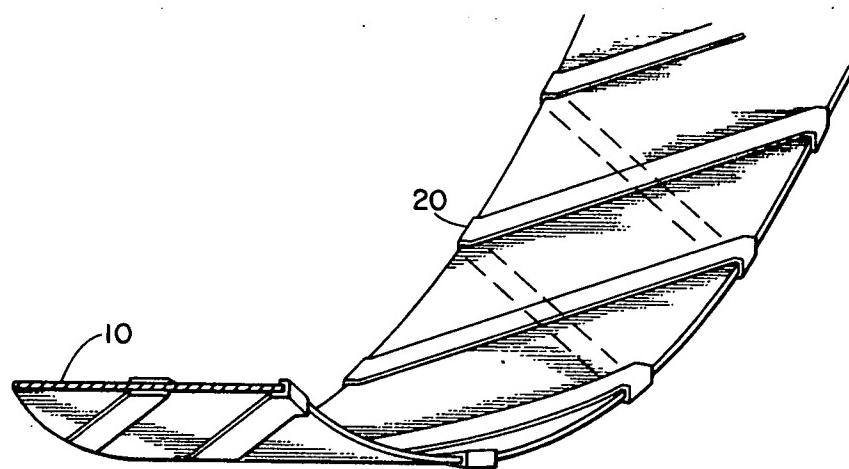


FIG. 7

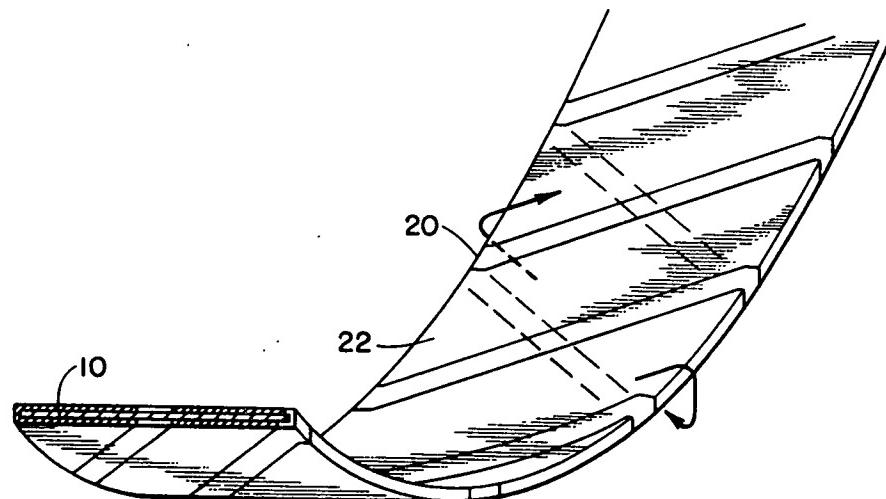


FIG. 8

TWISTED MULTIFILAMENT SUPERCONDUCTOR ORIGIN OF THE INVENTION

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

This invention is directed to a twisted multifilament intermetallic compound superconductive ribbon or tape. The invention is particularly concerned with producing such a material by controlling a diffusion reaction process.

Existing technology has provided commercially available, flexible, superconductive ribbon in the form of a substrate material having a brittle superconductive intermetallic compound, such as Nb₃Sn or V₃Ga, formed on the substrate by various means. These intermetallic compounds have the desirable characteristic of remaining in the superconductive state to higher values of magnetic field strength, temperature, and current densities than most other superconductive materials. However, thin sections are required to achieve the desired flexibility without damage because the compound is very brittle.

All known superconductors are subject to instabilities in their performance characteristics which limit their usefulness, unless certain steps are taken to reduce or eliminate these instabilities. The provision of a low resistance, high thermal conductance material in parallel and in intimate contact with the superconductor has been adequate for large, low current density applications. Other solutions are necessary for higher current density applications, such as very high field strength magnets.

The instabilities arise from magnetic flux penetrations called "flux jumps" which occur when the magnetic field strength at the superconductor forces shielded or pinned flux to move into or within the superconductor. These flux jumps are accompanied by local reversions to the resistive state. The severity of the effect is not solely determined by the value of the useful or "transport" current which must pass through the resistive region. It also depends on the value of the magnetization current, an induced circulating current, which may approach the critical current density.

Nontwisted current-sheet superconductors are subject to instabilities resulting from magnetization currents. The severity of the instability is strongly dependent on the rate of change of magnetic field at the conductor. Nontwisted current-sheet superconductors are totally unsuitable for alternating current applications.

For ductile superconductive alloys, such as NbTi, stability is achieved by dividing the superconductor into many fine filaments embedded in a copper matrix and then twisting the resulting composite conductor. The twist reduces the magnetization current loop path, and if sufficiently short twist pitches are used, the transport current can be made the limiting factor.

Thin ribbons or tapes of a superconductive material, such as Nb₃Sn or V₃Ga, present a different problem. A twisted Nb₃Sn filamentary structure has been produced in the form of cabled strands and suggested as strands in a matrix material. However, these methods cannot produce the desired flexibility of the conductor be-

cause of the extreme brittleness of the intermetallic compound. Winding of the unreacted niobium and tin materials and then reacting at high temperatures to form a compound in place has been used. However, this procedure suffers from the disadvantages of requiring high temperature insulation and results in a product that cannot be unwound or repaired. Winding of conductor shapes other than thin ribbon results in excessive tensile stresses in the outer fibers of the conductor.

10 This tends to destroy the brittle Nb₃Sn. The tensile stresses result from the difference in circumferential distance traversed by the outer and inner fibers of the conductor.

15 Removal of the superconductor to form filaments has been utilized in the prior art. However, this is a slow process, and it leaves unsupported edges of Nb₃Sn. Also the removal operation may damage adjacent sections of the material.

SUMMARY OF THE INVENTION

These problems have been solved by the present invention wherein the superconductor is divided and the current path twisted without physically distorting the ribbon. Prior to producing the superconductive compound a mask is formed on the base ribbon to selectively prevent the formation of the superconductive compound on predetermined portions of this substrate. The masked portions form the boundaries defining the filamentary structure and the twist characteristic. Subsequent diffusion reaction of the unprotected regions of the base ribbon and the other reaction constituents produces the superconductive compound only in the desired current path pattern.

OBJECTS OF THE INVENTION

It is, therefore, an object of the present invention to provide twisted filamentary current paths of a superconductive material without inherently placing tensile strains on a brittle material.

Another object of the invention is to form twisted filamentary current paths of superconductive intermetallic compounds having improved stability in that they are less susceptible to transition to the normal state than nontwisted and nonfilamentary intermetallic compounds.

A further object of the invention is to provide twisted filamentary current paths that are stable without sacrificing the flexibility of a ribbon conductor.

50 Still another object of the invention is to form twisted filamentary current paths of superconductive intermetallic compounds having supporting structure between the filaments.

These and other objects of the invention will be apparent from the specification which follows and from the drawing wherein like numerals are used throughout to identify like parts.

DESCRIPTION OF THE DRAWING

60 FIGS. 1 to 6 are sectional views illustrating the fabrication steps used to produce the superconductive ribbon of the present invention;

FIG. 7 is a perspective view of a ribbon with masking material forming twisted filamentary paths; and

65 FIG. 8 is a perspective view of a twisted filamentary superconductive ribbon constructed in accordance with the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring now to the drawings there is shown in FIG. 8 a twisted, multifilament superconductive ribbon of an intermetallic compound constructed in accordance with the present invention. A flexible base 10 of a suitable material, such as niobium, forms a substrate. This substrate is preferably in the form of a ribbon or tape a few hundredths of a millimeter thick and about 1.25 centimeters wide.

In order to make the ribbon shown in FIG. 8 the substrate 10 shown in FIG. 1 is first cleaned of surface impurities. This is accomplished by degreasing, immersing in an alkali solution, ultrasonically cleaning, or abrasive cleaning. It is further contemplated that other forms of cleaning may be utilized.

The substrate 10 is then coated all over with an intermediate masking material 12, such as copper, as shown in FIG. 2. This may be accomplished by evaporative coating, plating, roll bonding, or metallic spraying.

Predetermined portions of the masking material 12 are then selectively removed to form the inverse of the final mask. Regions 14 in FIG. 4 are exposed base and regions 16 are covered with the intermediate mask. Removal of the masking material in the regions 14 is preferably accomplished by a photo resist process.

In this process niobium ribbon 10 previously coated with masking material 12, such as copper or nickel, is additionally coated all over with suitable photo resist material 18, such as Kodak KPR-3, as shown in FIG. 2. The photo resist material is dried or baked. Then it is exposed to light selectively through previously prepared masks that are properly indexed on each side of the ribbon. In this manner the masks employed on each side of the ribbon are so positioned that continuous paths are formed across the faces of the ribbon and around the ribbon edges.

Development of the photo resist in suitable chemicals selectively removes the photo resist material leaving a protective coating over the portions which are not to be etched as shown in FIG. 3. After again drying or baking the etch resist material to harden it, the unwanted sections of the masking material 12 are removed in a suitable etchant, such as ferric chloride, exposing the niobium in the filament divider regions 14, but leaving the regions 16 covered with the masking material as shown in FIG. 4.

The final mask is formed on regions 20 of FIGS. 5 and 7 by heating the substrate 10 in an oxidizing atmosphere to a temperature between 200° C and 500° C. The temperature is preferably near 370° C. At this temperature oxides of niobium form on the exposed niobium base, the photo resist material 18 burns off, and the copper 12 remains. The heating is continued until an oxide layer forms on the region 14 of FIG. 4 to form the final mask 20 in FIGS. 5 to 8.

The intermediate mask on region 16 of FIG. 4 may then be removed or not. If the intermediate mask is copper it need not be removed.

A superconductive filament 22 shown in FIGS. 6 and 8 is then formed between the masked areas 20 by diffusion reaction. Copper will be displaced from the region 16 in the process.

By way of example, Nb₃Sn is formed by such a diffusion reaction between the exposed niobium ribbon and molten tin at temperatures between 900° C to 1200° C.

The Nb₃Sn is preferably formed between 930° C and 970° C. The masking material 20 shields the niobium from the tin and prevents the formation of the superconductive compound Nb₃Sn in the masked regions as shown in FIGS. 6 and 8.

The etchant resistant material also may be selectively applied by a suitably indexed printing process. In this manner only the desired masked regions on each side and edge of the coated ribbon have etchant resistant material applied.

Similarly, uncoated niobium ribbon may be masked with a plating resist material using a photo resist or printing process. The ribbon is then selectively plated in the unmasked sections of the ribbon. After removal of the plating resist to expose the bare niobium, the niobium oxide mask is formed. Then the diffusion reaction process is again used to form the Nb₃Sn superconductive compound.

In order to better illustrate the features of the invention a length of twisted multifilament niobium tin superconductive ribbon was made in accordance with the invention. Niobium ribbon 0.025 millimeters thick by 1.25 centimeters wide was cleaned in a sodium hydroxide solution for 10 minutes. The ribbon was then rinsed in distilled water and coated with a very thin film of copper in a vacuum chamber in which copper was evaporated and deposited on all surfaces of the niobium. This eliminates hydrogen contamination between the copper and the niobium.

The thinly copper coated strip was electroplated with copper to a copper thickness of about approximately 0.006 mm, rinsed, dried, and spray-coated on both sides and edges with Kodak KPR photo resist material. This was then air dried for 10 minutes and oven dried at 170° F for 10 minutes.

Previously prepared photographic film masks with approximately 10 lines per inch and with an opaque line to transparent spacing width ratio of approximately 1:3 were placed on each side of the ribbon with opposite slopes as viewed from one side. They were indexed to match opaque to opaque and transparent to transparent at the edges of the ribbon sandwiched between them. Thin transparent sheets, such as Lucite, were placed on each side of the sandwich array to prevent inadvertent misalignment. Exposure times of 5 1/2 minutes were used on each side. This relatively long exposure time was required because the KPR is most sensitive in the near ultraviolet part of the spectrum and the added Lucite absorbs ultraviolet light. After exposure, the ribbon was placed in Kodak photo resist developer for 2 1/2 minutes, rinsed, air dried for 10 minutes, and oven dried at a temperature of 170° F for 10 minutes.

The intermediate mask was formed by chemically etching away the unprotected copper to expose the niobium. The final mask of niobium oxide was formed by heating the ribbon in air to a temperature of 370° C for 5 minutes. A light chemical etch in dilute nitric acid removed any remaining photo etch resist material and copper oxide. The niobium oxide is a very stable compound and was unaffected.

The ribbon was suspended from a stainless steel rod in a Vycor tube which extended into a vertical furnace. The tube contained a tantalum crucible in the form of a tube with one closed end. A chromel-alumel thermocouple was attached to the outside of the Vycor tube. At the top end of the Vycor tube, out of the furnace, a transition to metal tubing was made, and in this sec-

tion provision was made for attaching a vacuum pump, gage, and argon gas supply. In addition, a sliding seal arrangement enabled vertical movement of the ribbon into and out of the furnace.

The apparatus was assembled, purged with argon gas, and pumped out several times to reduce contaminating residual gas levels. The apparatus was then pumped down to the low micron range of $5-10\mu$. The furnace was then turned on, and when the thermocouple indicated a temperature of 970°C had been reached, the ribbon was lowered into the tantalum crucible containing the molten tin, allowed to remain in the tin for $1\frac{1}{2}$ minutes, and withdrawn to just above the tin for an additional $1\frac{1}{2}$ minutes still in the high temperature region of the furnace. The ribbon was then withdrawn from the hot section of the tube and the furnace shut off.

After cooling to room temperature, the ribbon was removed from the apparatus and tested for superconductive properties. Tests indicated the transition temperature was greater than 17.95°K and the critical current at 0.6 telsa is 150 amperes. Metallographic examination showed no traces of copper remaining.

While the preferred embodiment of the invention has been shown and described it is contemplated that various modifications may be made without departing from the spirit of the invention or the scope of the subjoined claims.

What is claimed is:

1. A method of making a twisted multifilament superconductor comprising the steps of masking predetermined portions of a substrate to form a twisted configuration about said substrate, and forming a filament of a superconductive compound on said substrate between the masked portions.
2. A method of making a twisted multifilament superconductor as claimed in claim 1 wherein the superconductive compound filament is formed by diffusion reaction.
3. A method of making a twisted multifilament superconductor as claimed in claim 1 wherein the substrate is masked by coating the substrate with an intermediate masking material, removing said intermediate masking material in predetermined regions to expose the portions of the

substrate to be masked, and forming a mask in said regions by oxidizing the exposed substrate material therein.

4. A method of making a twisted multifilament superconductor as claimed in claim 3 wherein the mask is formed in the predetermined regions by heating the substrate after the intermediate masking material has been removed in the predetermined regions.

5. A method of making a twisted multifilament superconductor as claimed in claim 3 wherein the predetermined portions of the intermediate masking material are removed by a photo resist process.

6. A method of making a twisted multifilament superconductor as claimed in claim 5 wherein the predetermined portions of the intermediate masking material are removed by

covering the intermediate masking material with a photo resist material,

selectively exposing the photo resist material to light through masks that form continuous paths across the faces of the substrate and around the edges thereof,

developing the photo resist material to remove the same in said predetermined regions and provide a protective coating over said intermediate masking material in regions where the filament is to be formed, and

applying an etchant to the covered substrate to remove the intermediate masking material in said predetermined regions where said photo resist material has been removed.

7. A superconductive ribbon comprising a flexible substrate,

a superconductive compound in the form of filaments twisted about said substrate to form filamentary current paths, and

a mask between said filaments to support the same.

8. A superconductive ribbon as claimed in claim 7 wherein each twisted multifilament is an intermetallic compound of the substrate material formed by diffusion reaction.

9. A superconductive ribbon as claimed in claim 8 wherein the substrate is niobium.

10. A superconductive ribbon as claimed in claim 9 wherein the superconductive compound is Nb_3Sn .

* * * * *